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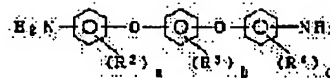
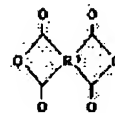
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(54) ORIENTING AGENT FOR LIQUID CRYSTAL

(57)Abstract:

PURPOSE: To obtain a stable pretilt angle in a specified range without disturbing the orientability of the liquid crystal by incorporating a polymer and imidized polymer obtd. by the reaction of tetracarboxylic acid dianhydride and diamine compd. expressed by specified formulae.

CONSTITUTION: This orienting agent for liquid crystal contains a polymer and/or its imidized polymer obtd. by the reaction of tetracarboxylic acid dianhydride expressed by formula I (R1 is a quadrivalent org. group) and a diamine compd. expressed by formula II (R2, R4 are univalent org. groups selected from methyl, ethyl, trifluoromethyl groups, R3 is a straight-chain and/or branched-chain alkyl group of 1-20 carbon number, (a), (c) are integers of 0 to 4, and (b) is an integer of 1 to 4). By this method, good orienting property is obtd. and a stable pretilt angle from 3 to 90 degree can be obtd. without disturbing the orienting property of the liquid crystal.



II

LEGAL STATUS

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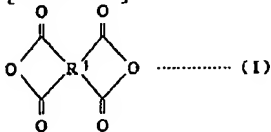
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CLAIMS

[Claim(s)]

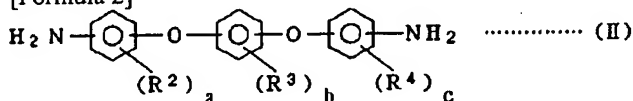
[Claim 1] The following general formula (I)

[Formula 1]



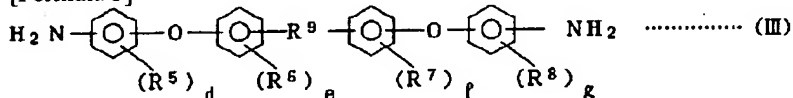
(-- here, R1 shows a tetravalent organic machine The tetracarboxylic dianhydride and the following general formula (II) which are expressed with)

[Formula 2]



(Here, R2 and R4 show the univalent organic machine chosen from a methyl group, an ethyl group, and a trifluoromethyl machine, and even if these are mutually the same, they may differ.) R3 shows the straight chain and/or branching alkyl group of carbon numbers 1-20. a and c show the integer of 0-4. b shows the integer of 1-4. And/or, the following general formula (III)

[Formula 3]



(Here, R5 and R8 show the univalent organic machine chosen from a methyl group, an ethyl group, and a trifluoromethyl machine, and even if these are mutually the same, they may differ.) R6 and R7 show the straight chain and/or branching alkyl group of carbon numbers 1-20, and even if these are mutually the same, they may differ. R9 shows the divalent organic machine chosen from -O-, -S-, -OCO-, -COO-, -NHCO-, -CONH-, -CO-, a methylene group, or the alkylene machine of carbon numbers 2-5. d and g show the integer of 0-4. e and f show the integer of 1-4. Liquid crystal orientation agent characterized by containing the polymer which the diamine compound expressed is made to react and is obtained, and/or its imide-ized polymer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to a liquid crystal orientation agent. In more detail, the stacking tendency of liquid crystal is good and is related with a liquid crystal orientation agent with a large pre tilt angle.

[0002]

[Description of the Prior Art] It is made a sandwich structure by the substrate with a transparent electrode which has the liquid crystal orientation film which consists of a polyimide etc. conventionally the nematic type liquid crystal which has a positive dielectric anisotropy, and the liquid crystal display element (TN type display device) which has a TN liquid crystal cell as the major axis of a liquid crystal molecule comes to be twisted between substrates continuously 90 degrees is known. The orientation of the liquid crystal in this TN type display device is formed with the liquid crystal orientation film with which rubbing processing was performed.

[0003] Since this TN type display device is inferior in contrast and a visual-sense dependency, the STN (Super twisted nematic) display device which is a liquid crystal display element excellent in contrast and the visual-sense dependency is developed recently. A STN display device uses the birefringence effect produced by twisting the major axis of a liquid crystal molecule continuously 180 degrees or more between substrates using what blended the chiral agent which is an optically active substance to nematic type liquid crystal as liquid crystal.

[0004]

[Problem(s) to be Solved by the Invention] However, when it produces using the liquid crystal orientation film which consists of a polyimide etc., since the pre tilt angle of a liquid crystal orientation film is small, a STN display device is difficult to be unable to twist liquid crystal 180 degrees or more between substrates, but to obtain a necessary display function.

[0005] for this reason, in order to carry out orientation of the liquid crystal in the case of the present STN display device, it is necessary to use the liquid crystal orientation film which carried out the method vacuum evaporation of the silicon dioxide of slanting, and formed it, and a manufacturing process is complicated -- etc. -- there is a problem

[0006] Moreover, since a STN display device carries out perpendicular orientation of the liquid crystal, it is required to process by the coupling agent which uses the substrate which carried out method deposition of the silicon dioxide of slanting, or has the surfactant and long-chain alkyl group of a fluorine system for a substrate. When a manufacturing process was complicated and it was not able to mass-produce, when the method vacuum evaporation of slanting is carried out, and a surfactant and a coupling agent were used, there was a problem that reliability was scarce.

[0007] The purpose of this invention solves the aforementioned conventional trouble, its stacking tendency of liquid crystal is good, and its pre tilt angle is large, and it is especially as an object for the liquid crystal orientation films of STN and SH display device to offer the liquid crystal orientation agent which can be used suitably.

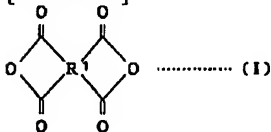
[0008]

[Means for Solving the Problem] As a result of inquiring wholeheartedly about the above-mentioned trouble, it became clear that the pre tilt angle stabilized without disturbing the stacking tendency of liquid crystal by making the diamine which contains three or more rings of benzene rings, and has an alkyl group in a side chain contain in polymer is obtained.

[0009] this invention is the following general formula (I).

[0010]

[Formula 4]

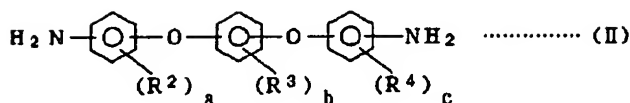


[0011] (Here, R1 shows a tetravalent organic machine.)

[0012] The tetracarboxylic dianhydride (henceforth "Compound I") and the following general formula (II) which are come out of and expressed

[0013]

[Formula 5]

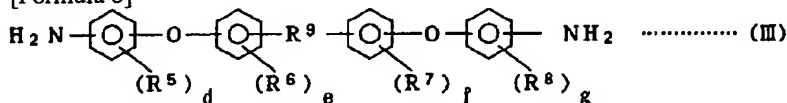


[0014] (Here, R² and R⁴ show the univalent organic machine chosen from a methyl group, an ethyl group, and a trifluoromethyl machine, and even if these are mutually the same, they may differ.) R³ shows the straight chain and/or branching alkyl group of carbon numbers 1-20. a and c show the integer of 0-4. b shows the integer of 1-4.

[0015] And/or, the following general formula (III)

[0016]

[Formula 6]



[0017] (Here, R⁵ and R⁸ show the univalent organic machine chosen from a methyl group, an ethyl group, and a trifluoromethyl machine, and even if these are mutually the same, they may differ.) R⁶ and R⁷ show the straight chain and/or branching alkyl group of carbon numbers 1-20, and even if these are mutually the same, they may differ. R⁹ shows the divalent organic machine chosen from -O-, -S-, -OCO-, -COO-, -NHCO-, -CONH-, -CO-, a methylene group, or the alkylene machine of carbon numbers 2-5. d and g show the integer of 0-4. e and f show the integer of 1-4.

[0018] It is related with the liquid crystal orientation agent characterized by containing the polymer (henceforth "the specific polymer I") which come out, and the diamine compound (henceforth "Compound II") expressed is made to react, and is obtained, and/or its imide-ized polymer (henceforth "the specific polymer II").

[0019] The compound I used in this invention is expressed with the above-mentioned formula (I). R¹ is equivalent to the residue which removed the acid-anhydride machine from Compound I among the above-mentioned formula.

[0020] As this compound I, for example Butane tetracarboxylic dianhydride, 1, 2, 3, 4-cyclobutane tetracarboxylic dianhydride, 1, 2 and 3, 4-cyclopentane tetracarboxylic dianhydride, 2, 3, 5-TORIKARUBOKI lion clo pentyl acetic-acid 2 anhydride, 3 and 5, 6-TORIKARUBOKISHI norbornane-2-acetic-acid 2 anhydride, 2, 3, 4, 5-tetrahydrofuran tetracarboxylic dianhydride, 1, 3, 3a, 4 and 5, 9b-hexahydro -5 -(tetrahydro-2, 5-dioxo-3-furanyl)- The [1 and 2-naphth c]-furan -1, 3-dione, The 5-(2, 5-dioxo tetrahydro FURARU)-3-methyl-3-cyclohexene -1, 2-dicarboxylic-acid 2 anhydride, Aliphatic series, such as the bicyclo [2, 2, 2]-OKUTO-7-en -2, 3 and 5, and 6-tetracarboxylic dianhydride, and alicycle group tetracarboxylic dianhydride; Pyromellitic acid 2 anhydride, - benzophenone tetracarboxylic dianhydride, 3, 3', and 3, 3', 4, and 4' 4, 4'-biphenyl sulfone tetracarboxylic dianhydride, 1, 4, 5, 8-naphthalene tetracarboxylic dianhydride, 2, 3 and 6, 7-naphthalene tetracarboxylic dianhydride, 3, 3', 4, 4'-biphenyl ether tetracarboxylic dianhydride, 3, 3', 4, 4'-dimethyl diphenyl silane tetracarboxylic dianhydride, 3,3',4,4'-tetraphenylsilane carboxylate dianhydride, 1, 2, 3, 4-furans tetracarboxylic dianhydride, 4, and 4'-screw (3, 4-dicarboxy phenoxy) diphenyl sulfide 2 anhydride, 4 and 4'-screw (3, 4-dicarboxy phenoxy) diphenylsulfone 2 anhydride, 4 and 4'-screw (3, 4-dicarboxy phenoxy) diphenyl propane 2 anhydride, 3, 3', 4, 4'-perfluoro isopropylidene tetracarboxylic dianhydride, 3, 3', 4, 4'-biphenyl tetracarboxylic dianhydride, screw (phthalic acid) phenyl phosphine oxide 2 anhydride, p-phenylene-screw (triphenyl phthalic acid) 2 anhydride, m-phenylene-screw (triphenyl phthalic acid) 2 anhydride, a screw (triphenyl phthalic acid) -4 and 4' -diphenyl-ether 2 anhydride, a screw (triphenyl phthalic acid) -4, and 4' -- aromatic tetracarboxylic dianhydride, such as -diphenylmethane 2 anhydride, can be mentioned Among these, butane tetracarboxylic dianhydride, 1, 2 and 3, 4-cyclobutane tetracarboxylic dianhydride, 2, 3, 5-TORIKARUBOKI lion clo pentyl acetic-acid 2 anhydride, the 5-(2, 5-dioxo tetrahydro FURARU)-3-methyl-3-cyclohexene -1, 2-dicarboxylic-acid 2 anhydride, 1, 3, 3a, 4, 5, 9b-hexahydro -5 -(tetrahydro-2, 5-dioxo-3-furanyl)- The [1 and 2-naphth c]-furan -1, 3-dione, - benzophenone tetracarboxylic dianhydride, 3, 3', and pyromellitic acid 2 anhydride, 3, 3', 4, and 4' 4, 4'-biphenyl tetracarboxylic dianhydride is desirable.

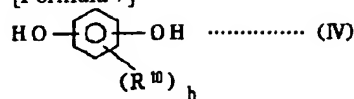
[0021] The compound II used in this invention is expressed with the above-mentioned formula (II) and/or the above-mentioned formula (III). This compound is obtained by returning a nitro group, after making the nitrobenzene compound which has the hydroxyl group of for example, phenol nature, and the halogen machine in which a reaction is possible in [one] a molecule, and the compound which has the hydroxyl group of phenol nature in [two] a molecule react under existence of an alkaline compound.

[0022] As a nitrobenzene compound which has a halogen machine in [one] a molecule For example, 4-chloronitrobenzene, 4-BUROMO nitrobenzene, 4-fluoro nitrobenzene, 4-iodine nitrobenzene, 3-chloronitrobenzene, 3-fluoro nitrobenzene, 3-iodine nitrobenzene, 2-chloronitrobenzene, 2-BUROMO nitrobenzene, 2-fluoro nitrobenzene, 2-iodine nitrobenzene, a 2-chloro-4-methyl nitrobenzene, A 4-chloro-3-methyl nitrobenzene, a 3-chloro-2-methyl nitrobenzene, A 5-chloro-2-methyl nitrobenzene, a 1-chloro-4-methyl nitrobenzene, A 2-chloro-4-ethyl nitrobenzene, a 4-chloro-3-ethyl nitrobenzene, A 3-chloro-2-ethyl nitrobenzene, a 5-chloro-2-ethyl nitrobenzene, A 1-chloro-4-ethyl nitrobenzene, a 2-chloro-4-trifluoromethyl nitrobenzene, A 4-chloro-3-trifluoromethyl nitrobenzene, a 3-chloro-2-trifluoromethyl nitrobenzene, a 5-chloro-2-trifluoromethyl nitrobenzene, a 1-chloro-4-trifluoromethyl nitrobenzene, etc. can be mentioned.

[0023] As a compound which has the hydroxyl group of phenol nature in [two] a molecule, it is the following general formula (IV), for example.

[0024]

[Formula 7]

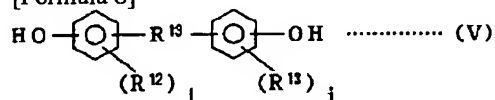


[0025] (Here, R¹⁰ shows the straight chain and/or branching alkyl group of carbon numbers 1-20.) h shows the integer of 1-4.

[0026] Or the following general formula (V)

[0027]

[Formula 8]



[0028] (Here, R¹¹ and R¹² show the straight chain and/or branching alkyl group of carbon numbers 1-20, and even if these are mutually the same, they may differ.) R¹³ shows the divalent organic machine chosen from ether oxygen, a phenylene group, and the alkylene machine of carbon numbers 1-10. i and j show the integer of 1-4.

[0029] ***** can be mentioned.

[0030] As a solvent used for the reaction of the nitrobenzene compound which has the hydroxyl group of these phenol nature, and the halogen machine in which a reaction is possible in [one] a molecule, and the compound which has the hydroxyl group of phenol nature in [two] a molecule, N-methyl-2-pyrrolidone, N, and N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, gamma-butyrolactone, a tetramethylurea, hexamethylphosphotriamide, etc. can be mentioned, for example.

[0031] As a basic compound used for a reaction, a potassium hydroxide, a sodium hydroxide, potassium carbonate, a sodium carbonate, a sodium hydride, a potassium metal, a sodium metal, a pyridine, a triethylamine, etc. can be mentioned.

[0032] Moreover, a phase transfer catalysis may be added in the case of a reaction, and a reaction may be promoted.

[0033] Reducing agents, such as zinc, iron, tin, tin chloride (II), a sodium sulfide (Na₂S, Na₂S₂, Na₂S_x), a sodium hydronium sulfide, a sodium hydrosulfite, and an ammonium sulfide, are advantageously used for reduction of the product of a reaction.

Moreover, palladium-carbon, platinum, a Raney nickel catalyst, platinum black, a rhodium-alumina, sulfuration platinum carbon, etc. can be made into a catalyst, for example, and it can also return by hydrogen gas, the hydrazine, the hydrochloric acid, etc.

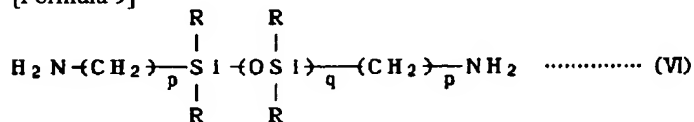
[0034] As a solvent of a reduction reaction, the ether, such as alcohol, such as ethanol, a methanol, and 2-propanol, diethylether, the methylethyl ether, and a methyl butyl ether, aqueous ammonia, toluene, water, a tetrahydrofuran, chloroform, or a dichloromethane is used, for example.

[0035] The specific polymer I makes Compound I and Compound II react, and is obtained. 0-150 degrees C of these reactions are usually preferably performed with the reaction temperature of 0-100 degrees C in an organic solvent.

[0036] Moreover, it is a book besides Compound II. As other diamine compounds, for example P-phenylene diamine, A - diamino diphenylmethane, and m-phenylenediamine, 4, and 4'4', 4'-diamino bibenzyl, A - diamino diphenyl sulfide, and 4 and 4'4', 4'-diaminodiphenyl sulfone, A 4 and 4'-diamino diphenyl ether, 1, 5-diamino naphthalene, The 3 and 3-dimethyl -4, a - diamino biphenyl, and 4'4', 4'-diamino benzanilide, A - diamino diphenyl-ether, and 4'3', 3'-diamino benzophenone, [3, and] 3, a - diamino benzophenone, and 4'4', 4'-diamino benzophenone, 2 and 2-screw [4-(4-amino phenoxy) phenyl] propane, 2 and 2-screw [4-(4-amino phenoxy) phenyl] hexafluoro propane, 2 and 2-screw (4-aminophenyl) hexafluoro propane, 2, and 2-screw [4-(4-amino phenoxy) phenyl] sulfone, 1, 4-screw (4-amino phenoxy) benzene, 1, 3-screw (4-amino phenoxy) benzene, A 1, 3-screw (3-amino phenoxy) benzene, 9, and 9-screw (4-aminophenyl)-10-hydronium anthracene, A 9 and 9-screw (4-aminophenyl) fluorene, 4, and 4'-methylene-screw (2-chloroaniline), A - (m-phenylene diisopropylidene) screw aniline, and 4 and 4'4', 4'-(p-phenylene diisopropylidene) screw aniline, 2, 2', 5 and 5'-tetrapod chloro -4, a 4'-diamino biphenyl, 2, 2'-dichloro -4, the 4'-diamino -5, a 5'-dimethoxy biphenyl, The aromatic diamine which has hetero atoms, such as aromatic diamine; diamino tetraphenylthiophenes, such as 3, 3'-dimethoxy -4, and a 4'-diamino biphenyl; 1 and 1-meta key silylene diamine, 1,3-propanediamine, a tetramethylenediamine, a pentamethylene diamine, A hexamethylenediamine, a heptamethylene diamine, an octamethylene diamine, Nonamethylene diamine, 4, and 4-diamino heptamethylene diamine, 1, 4-diamino cyclohexane, an isophorone diamine, a tetrahydro dicyclopentadienylene diamine, Aliphatic series or alicycle group diamines, such as hexahydro -4, 7-methano INDANIREN dimethylene diamine, and tricyclo [6, 2, 1, 02.7]-undecylene dimethyldiamine; the following general formula (VI)

[0037]

[Formula 9]



[0038] (the inside of a formula, and R -- the hydrocarbon group of carbon numbers 1-12 like aryl groups, such as cycloalkyl machines, such as alkyl groups, such as a methyl group, an ethyl group, and a propyl group, and a cyclohexyl machine, or a phenyl group, -- being shown -- p -- 1-3q -- each of 1-20 -- an integer is shown) etc. -- the diamino ORGANO siloxane expressed is

mentioned In these, a p-phenylene diamine, 4, and 4'-diamino diphenylmethane, 4 and 4' screw [- diamino diphenyl-ether, 2, and 2-] [4-(4-amino phenoxy) phenyl] propane, 9 and 9-screw (4-aminophenyl) fluorene 2 and 2-screw [4-(4-amino phenoxy) phenyl] hexafluoro propane, A - (m-phenylene diisopropylidene) screw aniline, and 2 and 2-screw (4-aminophenyl) hexafluoro propane, 4, and 4 '4, 4'-(p-phenylene diisopropylidene) screw aniline is desirable. These are independent or can be used combining two or more sorts.

[0039] this -- others -- use of the compound of a diamine -- all the inside of a diamine compound -- usually -- 0-90-mol % -- it is 0-80-mol % preferably

[0040] The operating rate of Compound I and all diamine compounds is 0.3 - 1.2 equivalence preferably [making the acid-anhydride machine of Compound I into 0.2 - 2 equivalence to the amino-group 1 equivalence in / all / a diamine compound], and more preferably.

[0041] If the specific polymer I generated at a reaction may be dissolved as the above-mentioned organic solvent used for a reaction, there will be especially no limit. For example, phenol system solvents, such as non-proton system polar-solvent;m-cresol, such as N-methyl-2-pyrrolidone, N, and N-dimethylacetamide, N.N-dimethylformamide, dimethyl sulfoxide, gamma-butyrolactone, a tetramethylurea, and hexamethylphosphortriamide, a xlenol, a phenol, and a halogenation phenol, can be mentioned. As for the amount of the organic solvent used, it is usually desirable to make it the total amount of Compound I and all diamine compounds become 0.1 - 30% of the weight to the whole quantity of a reaction solution.

[0042] The specific polymer II used for this invention is obtained by heating the above-mentioned specific polymer I, or imide-izing under existence of a dehydrating agent and an imide-ized catalyst. 60-200 degrees C of reaction temperature in the case of imide-izing by heating are usually 100-170 degrees C preferably. When reaction temperature is in advance of a reaction at less than 60 degrees C and 200 degrees C is exceeded, the molecular weight of the specific polymer II may fall greatly. Moreover, the reaction in the case of imide-izing under existence of a dehydrating agent and an imide-ized catalyst can be performed in said organic solvent. 0-180 degrees C of reaction temperature are usually 60-150 degrees C preferably. As a dehydrating agent, acid anhydrides, such as an acetic anhydride, a propionic anhydride, and an anhydrous trifluoroacetic acid, can be used. Moreover, as an imide-ized catalyst, although tertiary amine, such as a pyridine, a collidine, a lutidine, and a triethylamine, can be used, for example, it is not limited to these. As for the amount of the dehydrating agent used, it is desirable to consider as 1.6-20 mols to one mol of repeat units of the specific polymer I. Moreover, as for the amount of the imide-ized catalyst used, it is desirable to consider as 0.5-10 mols to one mol of dehydrating agents to be used.

[0043] In addition, it can use together to the grade to which the polymer which generates the alcohols which are poor solvents, ketones, ester, ether, halogenated hydrocarbons, and hydrocarbons does not deposit in the aforementioned organic solvent. As this poor solvent, for example Methyl alcohol, ethyl alcohol, Isopropyl alcohol, a cyclohexanol, ethylene glycol, A propylene glycol, 1, 4-butanediol, a triethylene glycol, An ethylene glycol monomethyl ether, an acetone, a methyl ethyl ketone, A methyl isobutyl ketone, a cyclohexanone, methyl acetate, ethyl acetate, Butyl acetate, an oxalic acid diethyl, a diethyl malonate, an ethyl lactate, diethylether, An ethylene glycol methyl ether, ethylene glycol ethyl ether, The ethylene glycol-n-propyl ether, the ethylene glycol-i-propyl ether, An ethylene glycol-n-butyl ether, an ethylene glycol wood ether, Ethylene glycol ethyl ether acetate, a diethylene-glycol wood ether, A tetrahydrofuran, a dichloromethane, 1, 2-dichloroethane, 1, 4-dichlorobutane, trichloroethane, chlorobenzene, o-dichlorobenzene, a hexane, a heptane, an octane, benzene, toluene, a xylene, etc. can be mentioned.

[0044] Thus, intrinsic-viscosity [η_{inh} = of the specific polymers I or II obtained (measurement)] is usually 0.05 - 5 dl/g preferably 0.05 to 10 dl/g about intrinsic viscosity on the following said conditions among $\ln \eta_{rel}/C$ and $C=0.5$ g/dl, 30 degrees C, and a N-methyl-2-pyrrolidone.)

[0045] Although the liquid crystal orientation agent of this invention contains the specific polymer I and/or II, in order to adjust the molecular weight of these specific polymers and to realize application nature to the optimal substrate, it may add a monoamine to reaction time.

[0046] In this case, as a monoamine to be used, an aniline, a cyclohexylamine, n butylamine, n-pentylamine, n-hexylamine, n-heptyl amine, n-octyl amine, n-nonyl amine, n-desyl amine, n-undecyl amine, n-dodecyl amine, n-tridecyl amine, n-tetradecylamine, an n-pentadecyl amine, an n-hexadecyl amine, an n-heptadecyl amine, n-octadecyl amine, n-EIKO sill amine, etc. can be mentioned.

[0047] Moreover, the liquid crystal orientation agent of this invention is the purpose which improves the adhesive property of the specific polymer I, and/or an II and a substrate, and can contain a functionality silane content compound.

[0048] As a functionality silane content compound, for example 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 2-aminopropyl trimethoxysilane, 2-aminopropyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane, 3-ureido propyltrimethoxysilane, 3-ureido propyl triethoxysilane, N-ethoxycarbonyl-3-aminopropyl trimethoxysilane, N-ethoxycarbonyl-3-aminopropyl triethoxysilane, N-triethoxy silyl PUROPURUTORI ethylene triamine, N-trimethoxysilylpropyl TORIECHIREN triamine, 10-trimethoxy ISHIRIRU - 1, 4, 7-TORIAZA decane, 10-triethoxy silyl - 1, 4, 7-TORIAZA decane, 9-trimethoxysilyl -3, 6-diaza nonyl acetate, 9-triethoxy silyl -3, 6-diaza nonyl acetate, N-benzyl-3-aminopropyl trimethoxysilane, N-benzyl-3-aminopropyl triethoxysilane, N-phenyl-3-aminopropyl trimethoxysilane, N-phenyl-3-aminopropyl triethoxysilane, N-screw (oxyethylene)-3-aminopropyl trimethoxysilane, N-screw (oxyethylene)-3-aminopropyl triethoxysilane, etc. are mentioned.

[0049] The liquid crystal display element obtained using the liquid crystal orientation agent of this invention can be manufactured by the following method.

[0050] First, the liquid crystal orientation agent of this invention is applied by the roll-coater method, the spinner method, print -

processes, etc., it heats at the temperature of 120-200 degrees C preferably, and 80-200 degrees C of paint films are made to form in the transparent electric conduction film side of the substrate in which the transparent electric conduction film was prepared. 0.001-1 micrometer of this paint film is usually 0.005-0.5 micrometers preferably.

[0051] Let the formed paint film be a liquid crystal orientation film by performing rubbing processing with the roll which twisted the cloth which consists of synthetic fibers, such as nylon.

[0052] As the above-mentioned substrate, the transparent substrate which consists of plastic film, such as glass, such as a float glass and a soda glass, a polyethylene terephthalate, a polybutylene terephthalate, polyether sulphone, and a polycarbonate, etc., for example can be used.

[0053] As the above-mentioned transparent electric conduction film, the NESA film which consists of SnO₂, the ITO film which consists of In₂O₃-SnO₂ can be used, and the photo etching method, the method using a mask, etc. are beforehand used for patterning of these transparent electric conduction films.

[0054] In order to make further the adhesive property of a substrate and a transparent electric conduction film, and a paint film into fitness on the occasion of the application of a liquid crystal orientation agent, a functionality silane content compound, titanate, etc. can also be beforehand applied on a substrate and a transparent electric conduction film.

[0055] the substrate in which the liquid crystal orientation film was formed counters so that the direction of rubbing may serve as a rectangular cross or antiparallel in a liquid crystal orientation film -- making -- the periphery between substrates -- a sealing compound -- a seal -- carrying out -- liquid crystal -- being filled up -- restoration -- a hole is closed, and it considers as a liquid crystal cell, and considers as a liquid crystal display element by making it rival so that the direction of rubbing of the liquid crystal orientation film of a substrate and the polarization direction are in agreement or may cross at right angles at the both sides,

[0056] As the above-mentioned sealing compound, the epoxy resin which contained the curing agent and the aluminum-oxide sphere as a spacer, for example can be used.

[0057] As the above-mentioned liquid crystal, pneumatic mold liquid crystal, smectic type liquid crystal, and the thing in which pneumatic mold liquid crystal is made to form also in it are desirable, for example, the Schiff base system liquid crystal, azoxy series liquid crystal, biphenyl system liquid crystal, phenylcyclohexane system liquid crystal, ester system liquid crystal, terphenyl system liquid crystal, biphenyl cyclohexane system liquid crystal, pyrimidine system liquid crystal, dioxane system liquid crystal, bicyclo octane system liquid crystal, cubane system liquid crystal, etc. are used. Moreover, cholesteric liquid crystal, such as KORESU chill chloride, KORESUTERIRUNONAETO, and cholesteryl carbonate, a tradename C-15, a chiral agent that is sold as CB-15 (Merck Ltd.) can also be added and used for such liquid crystal. Furthermore, p - Ferroelectric liquid crystals, such as DESHIROKISHI benzyldiene-p-amino-2-methyl butyl cinnamate, can also be used.

[0058] As a polarizing plate used for the outside of a liquid crystal cell, the polarizing plate which sandwiched the polarization film called H film which made iodine absorb by the cellulose acetate protective coat, or the polarizing plate which consists of the H film itself can be mentioned, carrying out extension orientation of the polyvinyl alcohol.

[0059]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not restricted to these examples.

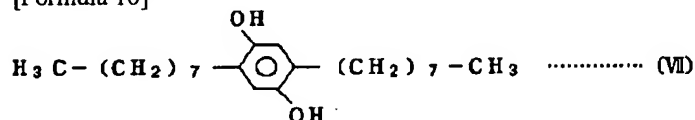
[0060] in addition, measurement of the pre tilt angle in an example -- [-- T. -- based on the method of a publication, it carried out to J.Schffer, et al., J.Appl.Phys., 19, and 2013] (1980) by the crystal rotation method using a helium-Ne laser beam

[0061] Moreover, stacking-tendency evaluation of a liquid crystal cell observed the existence of the unusual domain in the liquid crystal cell at the time of making voltage turn on and off with the polarization microscope, and judged that the case where there is no unusual domain was good.

[0062] The synthetic example 1 following formula (VII)

[0063]

[Formula 10]



[0064] It came out, 200g of compounds and 4-chloronitrobenzene 284g expressed were dissolved in 5000g of N.N-dimethylformamide, 150g of sodium hydroxides was added, and it was made to react at 150 degrees C for 8 hours. The obtained reaction mixture was poured out underwater and the reactant was settled. The product was fully washed with water and the nitro compound was obtained by recrystallizing in an acetone (60% of yield).

[0065] 100g of dinitro compounds obtained in the example 1 of synthetic example 2 composition was dissolved in ethanol 1000g, Pd/C 1g and 50g of hydrazine 1 hydrates were added, and it flowed back for 6 hours. After cooling to a room temperature, the sludge was carried out the ** exception, ethanol performed recrystallization, and Compound IIa was obtained (52% of yield).

[0066] The synthetic examples 32 and 3, 44.8g of 5-TORIKARUBOKI lion clo pentyl acetic-acid 2 anhydrides, and compound IIa103.2g were dissolved in 1332g of N-methyl-2-pyrrolidones, and it was made to react at a room temperature for 6 hours. Subsequently, the methanol of an overlarge was filled with reaction mixture, and the resultant was settled. Then, the methanol washed, it was made to dry at 40 degrees C under reduced pressure for 15 hours, and specific polymer Ia130.3g of intrinsic-viscosity 1.11 dl/g was obtained.

[0067] Specific polymer Ia30.0g obtained in the example 3 of synthetic example 4 composition was dissolved in 570g

gamma-butyrolactone, the 36.7g pyridine and the 31.3g acetic anhydride were added, and the imide-ized reaction reaction was carried out at 120 degrees C for 3 hours. Subsequently, reaction generation liquid was settled like the synthetic example 1, and specific polymer IIa25.3g of intrinsic-viscosity 1.04 dl/g was obtained.

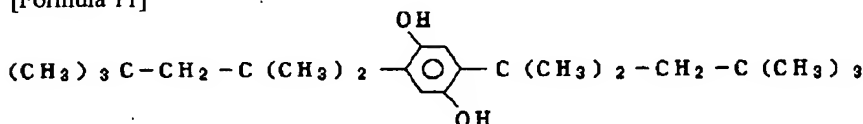
[0068] In the example 3 of synthetic example 5 composition, except having set p-phenylene diamine to 10.8g, and having set Compound IIa to 51.6g as a diamine compound, the specific polymer Ib was obtained like the synthetic example 3, the imide-ized reaction was further performed like the synthetic example 4 using this specific polymer Ib, and specific polymer IIb90.3g of intrinsic-viscosity 1.22 dl/g was obtained.

[0069] In the example 5 of synthetic example 6 composition, specific polymer Ic91.6g of intrinsic-viscosity 1.36 dl/g was obtained like the synthetic example 3 except having used the acid anhydride as 43.6g of pyromellitic acid 2 anhydrides.

[0070] The synthetic example 7 following formula (VIII)

[0071]

[Formula 11]



..... (VD)

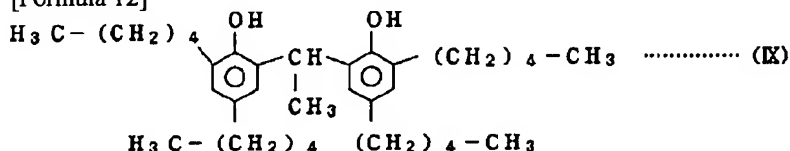
[0072] It came out, 200g of compounds and 4-chloronitrobenzene 284g expressed were dissolved in 5000g of N.N-dimethylformamide, 150g of sodium hydroxides was added, and it was made to react at 150 degrees C for 8 hours. The obtained reaction mixture was poured out underwater and the reactant was settled. The product was fully washed with water and the nitro compound was obtained by recrystallizing in an acetone (61% of yield). The nitro compound obtained like the synthetic example 2 after this was returned, and Compound IIb was obtained (50% of yield).

[0073] In the example 3 of synthetic example 8 composition, except having set p-phenylene diamine to 10.8g, and having set Compound IIb to 51.6g as a diamine compound, the specific polymer Ib was obtained like the synthetic example 3, the imide-ized reaction was further performed like the synthetic example 4 using this specific polymer Id, and specific polymer IIc90.2g of intrinsic-viscosity 1.12 dl/g was obtained.

[0074] The synthetic example 9 following formula (IX)

[0075]

[Formula 12]



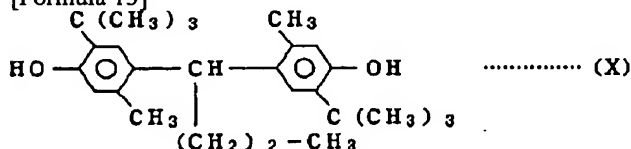
[0076] It came out, 200g of compounds and 4-chloronitrobenzene 192g expressed were dissolved in 5000g of N.N-dimethylformamide, 150g of sodium hydroxides was added, and it was made to react at 150 degrees C for 8 hours. The obtained reaction mixture was poured out underwater and the reactant was settled. The product was fully washed with water and the nitro compound was obtained by recrystallizing in an acetone (63% of yield). The nitro compound obtained like the synthetic example 2 after this was returned, and Compound IIIa was obtained (56% of yield).

[0077] In the example 3 of synthetic example 10 composition, except having set p-phenylene diamine to 10.8g, and having set Compound IIIa to 67.6g as a diamine compound, the specific polymer Ib was obtained like the synthetic example 3, the imide-ized reaction was further performed like the synthetic example 4 using this specific polymer Ie, and specific polymer IIe100.2g of intrinsic-viscosity 1.10 dl/g was obtained.

[0078] The synthetic example 11 following formula (X)

[0079]

[Formula 13]



[0080] It came out, 200g of compounds and 4-chloronitrobenzene 360g expressed were dissolved in 5000g of N.N-dimethylformamide, 150g of sodium hydroxides was added, and it was made to react at 150 degrees C for 8 hours. The obtained reaction mixture was poured out underwater and the reactant was settled. The product was fully washed with water and the nitro compound was obtained by recrystallizing in an acetone (60% of yield). The nitro compound obtained like the synthetic example 2 after this was returned, and Compound IIIb was obtained (51% of yield).

[0081] In the example 3 of synthetic example 12 composition, except having set p-phenylene diamine to 10.8g, and having set

Compound IIIb to 48.8g as a diamine compound, the specific polymer Ib was obtained like the synthetic example 3, the imide-ized reaction was further performed like the synthetic example 4 using this specific polymer If, and specific polymer IIf80.2g of intrinsic-viscosity 1.10 dl/g was obtained.

[0082] In the example 3 of synthetic example 13 composition, specific polymer immunoglobulin50.2g of intrinsic-viscosity 1.40 dl/g was obtained like the synthetic example 3 except having used only 21.6g for p-phenylene diamine as a diamine compound.

[0083] The polymer Ia obtained in the example 3 of example 1 composition was dissolved in 72g of gamma-butyrolactone, it considered as the solution of 4 % of the weight of solid-content concentration, this solution was filtered with the filter of 1 micrometer of apertures, and the liquid crystal orientation agent solution was prepared. On the glass substrate with a transparent electrode which consists this solution of an ITO film, the spinner was used and applied to the transparent-electrode side for 3 minutes by rotational frequency 3000rpm, it dried at 180 degrees C for 1 hour, and the paint film of 0.05 micrometers of dryness thickness was formed. The rubbing machine which has the roll which twisted the cloth made of nylon around this paint film performed rubbing processing by the 1cm [second] traverse speed of rotational frequency 500rpm of a roll, and a stage. Next, it piled up, the substrate of a couple was stuck by pressure so that a liquid crystal orientation film surface might face and the direction of rubbing might moreover become antiparallel, and each rim which has the liquid crystal orientation film of a substrate with which rubbing processing of the couple was carried out was made to harden adhesives, after carrying out the screen-stencil application of the epoxy resin adhesive containing an aluminum-oxide sphere with a diameter of 17 micrometers. Subsequently, from the liquid crystal inlet, after being filled up with pneumatic mold liquid crystal (1565 the Merck Co. make, ZLI- 2293) between the substrates of a couple, the liquid crystal inlet was closed with epoxy system adhesives, and lamination and the liquid crystal display element were produced so that the polarization direction of a polarizing plate might be in agreement with the direction of rubbing of the liquid crystal orientation film of each substrate in a polarizing plate by both sides of the outside of a substrate. the stacking tendency of the obtained liquid crystal display element -- good -- liquid crystal -- ZLI- when the pre tilt angle when being referred to as 1565 and 2293 was measured, they were 89 degrees and 88 degrees, respectively

[0084] In two to example 7 example 1, except having used the specific polymers IIa, IIb, Ic, IId, IIf, and IIf obtained in the synthetic examples 4, 5, 6, 8, 10, and 12, the liquid crystal display element was produced like the example 1, the stacking tendency and pre tilt angle of the liquid crystal display element were measured, and the result was shown in Table 1.

[0085]

[Table 1]

実施例	重合体	プレチルト角 (度)		液晶配向性
		ZLI-1565	ZLI-2293	
2	I I a	8 8	8 9	良好
3	I I b	6. 8	7. 6	同上
4	I c	8. 3	9. 3	同上
5	I I d	7. 2	7. 3	同上
6	I I e	10. 2	12. 3	同上
7	I I f	6. 0	6. 8	同上

[0086] although the stacking tendency of the obtained liquid crystal display element was good when the liquid crystal display element was produced like the example 1 except having used the specific polymer immunoglobulin obtained in the example 13 of example of comparison 1 composition and the evaluation was performed -- liquid crystal -- ZLI- when the pre tilt angle when being referred to as 1565 and 2293 was measured, they were 0.9 degrees, 1.1 degrees, and a low thing, respectively

[0087]

[Effect of the Invention] According to the liquid crystal orientation agent of this invention, the pre tilt angle of 3 - 90 degrees stabilized without the stacking tendency having been good and disturbing the stacking tendency of liquid crystal is discovered, and a liquid crystal orientation film suitable as STN or an object for SH display devices is obtained. Moreover, the liquid crystal display element which has the liquid crystal orientation film formed using the liquid crystal orientation agent of this invention can be used by choosing the liquid crystal to be used suitable also for a subacute-bacterial-endocarditis display device, a strong dielectric display device, and an antiferroelectric display device. Furthermore, the liquid crystal display element which has the orientation film formed using the liquid crystal orientation agent of this invention is excellent in the stacking tendency and reliability of liquid crystal, and can be used effective in various equipments, for example, is used for display, such as a desktop computer, a wrist watch, a clock, the coefficient plotting board, a word processor, a personal computer, and a liquid crystal television.

[Translation done.]

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